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ELECTRON-HYDROGEN IONIZATION: ASYMPTOTIC FORM OF THE WAVE FUNCTION AND THE THRESHOLD BEHAVIOUR OF THE CROSS SECTION

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the Asymptotic Form of the Wave Function
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Abstract

The asymptotic form of the wave function for (S-wave) electron-hydrogen ionization deduced by Peterkop and by Rudge and Seaton is examined and found not to obey the correct boundary condition at $r_1 = r_2$. In addition the quantity by which it differs from being an exact solution becomes infinitely large as $r_1 \to r_2$. On the basis of the zeroth order problem of the nonadiabatic theory of electron-hydrogen scattering other solutions are shown to exist. Within this approximation we show how a fully satisfactory solution of the Schrödinger equation can be constructed, and we indicate that it leads to an $E^{3/2}$ threshold law for ionization. Furthermore, it lends itself to a natural generalization for the asymptotic form of the full S-wave problem which continues to suggest a nonlinear threshold dependence for the complete problem.

The problem of the ionization of atomic hydrogen by electron impact is a fundamental problem dealing with the separated configuration of three charged particles. In addition to its theoretical interest, the problem is of considerable current importance because recent observations of the elastic resonances in electron-hydrogen scattering[1] are limited in accuracy because of the uncertainty of the shape of the ionization cross section. Specifically, this inaccuracy stems from the uncertainty of the nature of the threshold energy dependence of the ionization cross section, whose starting point is a key reference point in determining the experimental energy scale.

Although there have been numerous approximate calculations of the ionization cross section of atomic hydrogen by electron impact, it is only comparatively recently that attempts have been made to put this problem on a more rigorous theoretical footing. Peterkop[2] and somewhat later, but largely independently, Rudge and Seaton[3,4] have derived an asymptotic form of the wave function. This asymptotic form can then be used to determine a phase factor which must be known in order that an independently derived relation between direct and exchange ionization amplitudes[5] be useful. In addition this asymptotic form is, in the important region of configuration space, proportional to the complex conjugate of a function Φ, a product of two Coulomb waves whose charges depend on the vector velocities of the outgoing particles, which is the basis upon which the linear threshold law is deduced.[6]

The purpose of this note is to point out inadequacies in the above asymptotic form, and to show by means of a simpler model that the neglect of certain terms which must be made in deriving it is not justified. The two arguments taken together strongly indicate that the asymptotic form is not correct. This in turn has obvious negative implications about the above mentioned phase factor and about the derivation of a linear threshold law.

We restrict ourselves to the total S-wave system for which the Schrödinger equation can be written (energies in rydbergs, lengths in Bohr radii):

$$\left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2}\right)\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}} + \frac{2}{r_1} + \frac{2}{r_2} - \frac{2}{r_{12}} + E\right]\psi(r_1, r_2, \theta_{12}) = 0 \tag{1}$$

where ψ is $r_1\, r_2$ times the S-wave function Ψ. The previous analyses[2,3] have been made in terms of hyperspherical coordinates:

$$\rho \equiv (r_1^2 + r_2^2)^{1/2} \tag{2a}$$

$$\alpha \equiv \tan^{-1}(r_2/r_1) . \tag{2b}$$

In terms of these coordinates, the S-wave Schrödinger equation becomes

$$\left[\frac{\partial^2}{\partial\rho^2} + \frac{1}{\rho}\frac{\partial}{\partial\rho} + \frac{1}{\rho^2}\frac{\partial^2}{\partial\alpha^2} + \frac{2}{\rho}W(\alpha, \theta_{12}) + \frac{4}{\rho^2\sin^2 2\alpha}\frac{1}{\sin\theta_{12}}\frac{\partial}{\partial\theta_{12}}\sin\theta_{12}\frac{\partial}{\partial\theta_{12}} + E\right]\psi(\rho, \alpha, \theta_{12}) = 0 , \tag{3}$$

where

$$W'(\alpha,\theta_{12}) = (\sin\alpha)^{-1} + (\cos\alpha)^{-1} - (1-\sin 2\alpha\cos\theta_{12})^{-1/2} \quad (4)$$

The asymptotic form of references 2 and 3, can be derived from (3) by neglecting all terms which depend on ρ^{-2}. In this way Equation (3) becomes an ordinary differential equation in ρ whose solution depends only parametrically on the remaining coordinates α and θ_{12}. In particular, that solution which represents an outgoing radial current <u>in this approximation</u> is

$$\lim_{\rho\to\infty} \psi_c = \frac{f(\alpha,\theta_{12})}{\rho^{1/2}} \exp\left\{i\left[\sqrt{E}\rho + \frac{W\ln(\sqrt{E}\rho)}{\sqrt{E}}\right]\right\}, \quad (5)$$

where $f(\alpha,\theta_{12})$ is a function whose specification we need not here consider. If one operates on this function with the ρ^{-2} terms that were neglected in Equation (3), one finds the leading order term is

$$\frac{-1}{\rho^2}\left[\left(\frac{\partial W}{\partial\alpha}\right)^2 + \frac{4}{\sin^2 2\alpha}\left(\frac{\partial W}{\partial\theta_{12}}\right)^2\right]\left(\frac{\ln\sqrt{E}\rho}{\sqrt{E}}\right)^2 \psi_c . \quad (6)$$

This remainder term being also essentially of order ρ^{-2} appears consistent with the neglect of such terms in the first place. (But see below.)

It should be noted that this argument is not foolproof, because it is possible that (a) a solution with asymptotic form of Equation (5) satisfying all other required boundary conditions does not exist, (b) there is an other solutions for which the terms in question <u>cannot</u> be neglected. Indeed if (a) is the case, then (b) follows.

If (5) were the correct asymptotic form, it would have to be valid for both space symmetric (singlet) and space antisymmetric (triplet) solutions. We shall consider the singlet case in this paragraph. The phase in (5) depends on W. But from (4), W is proportional to the total potential energy and therefore has singularities where the potential has singularities; one of these is at $r_{12} = 0$, which can occur for large values of $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ where Equation (5) is supposed to be valid. Nor can anything in $f(\alpha, \theta_{12})$ cancel this singularity since the W term is multiplied by a function of ρ. However, a correct quantum mechanical solution has a cusp where the potentials are singular.[7]

Of even greater significance is the fact that the quantity by which this function differs from being an exact solution, the expression (6), is (for a given ρ) even more singular than the potential itself at $\underset{\sim}{r}_1 = \underset{\sim}{r}_2$.

Peterkop[8] has stated that this singularity recedes to infinity by which we presume he means that since (5) represents an asymptotic expansion, the region where the asymptotic form becomes valid demands ρ be indefinitely large as $\underset{\sim}{r}_1 \to \underset{\sim}{r}_2$. This argument is circular: there is a correct asymptotic form of the wave function including the region $\underset{\sim}{r}_1 = \underset{\sim}{r}_2$; the problem is, given the Schrödinger equation as a partial differential equation, to find that solution. When one has found that solution, one can inquire as to whether it is close to another (approximate) solution of (5) which does not obey that boundary condition. In fact the form of (5) is reminiscent of a WKB type of approximation, and the divergence of the phase along singularities of the potential is a characteristic defect of that approximation. The crucial question of whether a WKB description is valid depends on the energies and masses of the particles involved. We shall talk of the energy dependence below, but it is clear that the approximation is much more compelling for, say, proton-hydrogen ionization than for e-H ionization.

We shall next show by considering a simplified model that there almost certainly are solutions of (3) for which one cannot neglect ρ^{-2} terms even in the asymptotic region. The model consists of replacing W in Equation (3) by its spherical average $W_o = (1/2) \int W \sin \theta_{12} d\theta_{12}$:

$$W_0 = \begin{cases} 1/\sin\alpha & r_1 > r_2 \\ 1/\cos\alpha & r_1 < r_2 \end{cases} \tag{4a}$$

It is clear that going through the same arguments which led to ψ_c would in this case lead to a solution with asymptotic form

$$\lim_{\rho\to\infty} \psi_c^{(0)} = \frac{f_0(\alpha)}{\rho^{1/2}} \exp\left\{ i\left[\sqrt{E}\rho + \frac{W_0 \ln(\sqrt{E}\rho)}{\sqrt{E}}\right]\right\}. \tag{5a}$$

Here the diverging phase along $\underset{\sim}{r}_1 = \underset{\sim}{r}_2$ is transformed into a cusp (discontinuity of slope) along $r_1 = r_2$, but in essence inadequacy remains.[7] In addition we can here write down exact solutions neglecting no terms in W_o equation. An example of such a solution is:

$$\psi_{q_1,q_2}^{(0)} = e^{iq_1\rho\cos\alpha} F_{q_2}^{(+)}(\rho\sin\alpha) \tag{7}$$

where

$$q_1^2 + q_2^2 = E \tag{8}$$

and $F^{(+)}_{q_2}(\chi)$ is the $\ell = 0$ outgoing wave Coulomb function:

$$\lim_{\chi \to \infty} F^{(+)}_q(\chi) = e^{i(q\chi + q^{-1}\ln\chi + \sigma_0)} \tag{9}$$

Note that for $\Psi^{(o)}_{q_1 q_2}$ to be a solution, one cannot neglect the $\rho^{-2}\partial^2/\partial\alpha^2$ term in the model Schrödinger equation. In particular $\partial^2/\partial\alpha^2$ brings down ρ^2 which cancels the ρ^{-2} factor making this term non-vanishing even in the asymptotic region. (Thus this term, in spite of being formally of the order ρ^{-2}, is in fact more important than the Coulombic potential term.)

Considering the totality of solutions (all q_1, q_2 for a given E), one cannot say beforehand whether the sum yields a function for which one can neglect the $\partial^2/\partial\alpha^2$ term. In the case of short range forces the elementary ionization (S-wave) solutions are

$$e^{ik_1 r_1} e^{ik_2 r_2} = e^{ik_1\rho\cos\alpha} e^{ik_2\rho\sin\alpha}, \tag{10}$$

for which one can also not neglect the $\partial^2/\partial\alpha^2$ term. Nevertheless when one sums the totality of such solutions one arrives at a function[3]

$$\lim_{\rho \to \infty} \Psi_S = \frac{f_S(\alpha)}{\rho^{1/2}} e^{i\sqrt{E}\rho}, \tag{11}$$

for which one can neglect the $\rho^{-2}\partial^2/\partial\alpha^2$ derivative. In the case of the Coulomb forces, however, the inadequacy of (5) and (5a) along $\underset{\sim}{r}_1 = \underset{\sim}{r}_2$ ($r_1 = r_2$) shows that the composite solution will not allow this second derivative to be neglected. (Notice that (11) does not contain these difficulties along the $\underset{\sim}{r}_1 = \underset{\sim}{r}_2$ boundary.)

When the model Schrödinger equation is written in terms of r_1 and r_2,

$$\left(\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \frac{2}{r_2} + E \right) \Phi_0^{(0)}(r_1, r_2) = 0 , \qquad r_1 > r_2 , \tag{12}$$

it can be seen to be the zeroth order problem of the non-adiabatic theory of electron-hydrogen scattering.[9] For energies below the ionization threshold ($E < 0$) exact solution can be written in terms of exact separable solutions:

$$\Phi_0^{(0)} = A \frac{\sin kr_1}{k} R_{1s}(r_2) + \sum_{n=1} C_n e^{ik_n r_1} R_{ns}(r_2) + \int_0^\infty C(\varkappa_2) e^{-\varkappa_1 r_1} F_{\varkappa_2}(r_2) \, d\varkappa_2 , \tag{13}$$

where

$$E = k_n^2 - n^{-2} = -\varkappa_1^2 + \varkappa_2^2 , \tag{8a}$$

and F refers to the $\ell = 0$ Coulomb wave function regular at the origin. The point is that the coefficients in (13) are determined by the condition the singlet or triplet boundary condition along $r_1 = r_2$ be smoothly satisfied.[7] Utilizing the continuity conditions, and the conservation of current, we have analytically shown in both the singlet and triplet cases that for energies near ionization threshold $C_n \propto n^{-3/2}$, which implies[10] that the threshold dependence is proportional to $E^{3/2}$ for the zeroth order problem.

Above threshold it would be tempting to augment (13) with terms of the form

$$\int_0^{\sqrt{E}} C(q_2)\, e^{iq_1 r_1}\, F_{q_2}(r_2)\, dq_2 \quad ,$$

with the requirement that $C(q_2)$ be chosen so that the boundary condition along $r_1 = r_2$ be satisfied. However, such terms do not obey the requirement of outgoing current for the inner particle (r_2). It is clear in fact that this asymptotic condition demands a sum of functions of the type of Eq. (10):

$$\int_0^{\sqrt{E}} C(q_2)\, e^{iq_1 r_1}\, F^{(+)}_{q_2}(r_2)\, dq_2 \quad , \tag{14a}$$

with $C(q_2)$ still determined by the boundary condition along $r_1 = r_2$; but unless a miracle happened this function will not be well-behaved at $r_2 = 0$. The conclusion from all of this is that the expansion in terms of separable products (on the energy shell) is manifestly not complete in the ionization region. One thing that can be done is to imagine a variational counterpart of (14a) of the form, say,

$$\int_0^{\sqrt{E}} C(q_2)\, e^{iq_1 r_1}\, F^{(+)}_{q_2}(r_2)\left[1 - e^{-\beta(q_2) r_2}\right] dq_2 \tag{14b}$$

The boundary condition along $r_2 = 0$ is now automatically satisfied and the double set of coefficients $\beta(q_2)$ and $C(q_2)$ are now determined by the condition that (14b) be a solution of the zeroth order problem and that it satisfy the boundary condition that $r_1 = r_2$. In this way we will not have avoided the boundary condition requirement along $r_1 = r_2$ and the resultant solution will not be subject to the criticism of (and therefore will be different from) Eq. (5a).

The individual solutions in (14) describe, in a clear way, the quantum mechanics of the physical situation. The scattered particle moves as an outgoing (free) spherical wave whereas the inner particle moves in the Coulomb field of the nucleus. That this continues to be the case when one considers the full (W) interaction has not been proven. In fact the semi-classical argument (which corresponds to this function Φ^* in the first approximation) contends that the outer particle sees an r_1^{-1} potential coming from the fact it sees (in the first approximation) a dipole field of the nucleus and the inner electron, the dipole moment of which expands as r_1 itself (due to the inner and outer particle coming out with a constant ratio of their velocities). We, however, consider this argument to be erroneous, because from the quantum mechanical viewpoint in order to prepare an incident beam of a given energy, one requires a longer and longer wave train. Thus the emerging particles are described by spherical waves, and what the outer particle sees is not an inner particle in a definite orbit but a smeared out probability amplitude which has the effect ultimately of screening the outer electron from the nucleus. This consideration is particularly relevant near threshold where the wave lengths of both emergent particles are large. This is the physical basis upon which we believe that not only is the asymptotic form of ψ_c in Equation (5) not completely correct, which we have already shown, but substantially incorrect in the threshold region.

Finally, these considerations show that one cannot neglect the $\rho^{-2}\sin^{-1}\theta_{12}\,\partial/\partial\theta_{12}(\sin\theta_{12})\,\partial/\partial\theta_{12}$ term in the full S-wave problem anymore than one can neglect the $\rho^{-2}\,\partial^2/\partial\alpha^2$ term in the zeroth order problem. In fact we can find solutions in the presence of this term providing we retain W_0 in place of W. A typical solution is $h_\ell(q_1r_1)F^{(+)}_{\ell q_2}(r_2)\,P_\ell(\cos\theta_{12})$ where h_ℓ and $F^{(+)}_{\ell q_2}$ are the ℓth spherical Hankel function and outgoing wave Coulomb wave function respectively. The most general such wave function incorporates the features of the previous mathematical and physical arguments, and thus we believe it represents the correct asymptotic form of the S-wave function:

$$\lim_{r_1>r_2\to\infty}\psi=\sum_{\ell=0}^{\infty}P_\ell(\cos\theta_{12})\int_0^{\sqrt{E}}C_\ell(q_2)\,h_\ell(q_2r_1)\,F^{(+)}_{\ell q_2}(r_2)\,dq_2\;. \tag{21}$$

This form is θ_{12} dependent, of course, but being a product of free (spherical) waves and Coulomb waves it would suggest a nonlinear threshold law for ionization.

A C K N O W L E D G E M E N T S

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References and Footnotes

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2. R. K. Peterkop, Optics and Spectroscopy, 13, 87 (1962). Further references to this author's work are given here and in Reference 3.

3. M. R. H. Rudge and M. J. Seaton, Proc. Roy. Soc. (London) A283, 262 (1965). This paper contains a fairly complete bibliography of the literature on the subject. Cf. in particular G. Wannier, Phys. Rev. 90, 817 (1953) for a semi-classical treatment.

4. M. R. H. Rudge and M. J. Seaton, Proc. Phys. Soc. (London), 83, 680 (1964).

5. R. K. Peterkop, Proc. Phys. Soc. (London), 77, 1220 (1961).

6. If one assumes the asymptotic form of PRS to be correct, the argument for the linear threshold law as we have had to reconstruct it, although believable, is not rigorous. It is somewhat unfortunate that in Ref. 4 the argument is never given nor is any statement made of how rigorously the result is considered to have been derived. If, as we shall argue, their asymptotic form is not correct, it is not clear that the formal expression for the ionization amplitude from which they start is correct; but even if it is correct, the further arguments are completely invalid.

7. T. Kato, Commun. Pure Appl. Math. 10, 151 (1957). For other references and a brief historical introduction see R. T. Pack and J. O. Hirschfelder, Univ. of Wisconsin Report WIS-TCI-123 (1965, unpublished). In the zeroth order problem (the one associated with W_0) the potential has a cusp, so that the correct solution must be continuous with a continuous first derivative, which Equation (5a) is not.

8. R. K. Peterkop, Zh. Eksperim. i Teor. Fiz. (USSR) 43, 616 (1962). (English transl. Soviet Phys. JETP 36, 1256, (1959)).

9. A. Temkin, Phys. Rev. 130, 126 (1962).

10. K. Omidvar, private communication. The derivation is not rigorous because it requires extrapolating $n^{-3/2}$ to $k^{3/2}$ for the ionization coefficients above threshold. This extrapolation has not been rigorously proven.

11. J. W. McGowan, M. A. Fineman, E. M. Clarke, and H. P. Hanson (to be published). It should be noted that Wannier, Reference 3, also derived a non-linear threshold dependence.